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## XIV.

CONTRIBUTION FROM THE SALISBURY LABORATORY OF  
THE WORCESTER POLYTECHNIC INSTITUTE.

ON THE FORMATION OF CHLOR AND BROMBENZOIC  
ANHYDRIDES.

BY GEORGE D. MOORE AND DANIEL F. O'REGAN.

Presented June 14, 1893.

IN a previous paper\* entitled "On the Formation of the Anhydrides of Benzoic and substituted Benzoic Acids," we have shown that by the action of phosphorpentoxide upon benzoic and mono-nitrobenzoic acids in the presence of an excess of benzol at the boiling temperature the anhydrides of these *acids* are produced. Further investigation has shown that the monochlor and monobrombenzoic acids behave in a similar manner.

The process by which the chlor and bromanhydrides are prepared is essentially the same as that already described under the nitro compounds. The only difference worthy of note consists in using rather a larger quantity of phosphorpentoxide, and in boiling the mixture somewhat longer. Thus, whereas in the case of the nitro anhydrides we employed equal weights of acid and phosphorpentoxide, boiling with benzol for four hours, the halogen compounds require about one fifth excess of phosphorpentoxide and five to six hours boiling.

I. *Orthochlorbenzoic Anhydride.*

The orthochlorbenzoic acid necessary for the preparation of this substance was made according to the method described by Anschütz and one of us,† by treating salicylic acid with phosphorpentachloride, and, after rectifying the product *in vacuo*, decomposing it by distillation at ordinary atmospheric pressure.

10 grams of orthochlorbenzoic acid, prepared in this manner and melting at 137°, were heated with 12 grams of phosphorpentoxide

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\* These Proceedings, XXVII. 93.

† Ann. Chem., CCXXXIX. 326.

and about 200 c. c. of dry benzol under a reverse condenser for about six hours. The light brown mother liquor was then decanted hot from the insoluble residue, the latter boiled up with fresh benzol, this extract added to the first, and the whole concentrated to a small volume. No precipitate appearing, the concentration was continued until a thick crust was obtained. This, after crystallization from ligroine, yielded an abundance of fine white needles, which melted at  $141^{\circ}$  and gave on analysis the following values: —

0.1452 gr. substance gave 0.1425 gr. AgCl.  
0.1346 gr. gave 0.2798 gr. CO<sub>2</sub> and 0.0348 gr. H<sub>2</sub>O.

Calculated for		Found.
C <sub>6</sub> H <sub>4</sub>	{ (1) Cl (2) CO	
	>O	
C <sub>6</sub> H <sub>4</sub>	{ (2) CO (1) Cl	
C	56.96	56.70
H	2.71	2.87
Cl	24.07	24.28

The orthochlorbenzoic anhydride is very soluble in alcohol, ether, chloroform, and benzol, less soluble in ligroine. From this last it is precipitated in the form of glittering white needles. Water and alkalies attack it slowly in the cold, more readily on heating.

## II. *Metachlorbenzoic Anhydride.*

After numerous fruitless attempts to prepare metachlorbenzoic acid from benzoic acid by the method of Hübner and Weiss ;\* we had recourse to that of Sandmeyer,† which proved perfectly satisfactory. For the preparation of the acid on a laboratory scale this method leaves little to be desired.

10 grams of the pure acid melting at  $153^{\circ}$  were boiled up under a reverse condenser with 12 grams of phosphorpentoxide and an excess of benzol for six hours. The decanted mother liquor, together with benzol washings from the phosphoric residue, were concentrated, and the white crystalline mass which separated out, purified by pressing between filters and recrystallizing from fresh benzol. The substance thus obtained did not show a constant melting point. It was therefore washed several times with dilute potash, dried, and again crystallized. It now melted constant at  $89^{\circ}$ , and gave on analysis the following: —

\* Ber. d. ch. G., VI. 175.

† Ber. d. ch. G., XVII. 1634.

0.1900 gr. substance gave 0.1833 gr. AgCl.  
 0.1944 gr. gave 0.4052 gr. CO<sub>2</sub> and 0.0497 gr. H<sub>2</sub>O.

Calculated for		Found.
C <sub>8</sub> H <sub>4</sub>	{ (1) Cl (3) CO >O C <sub>8</sub> H <sub>4</sub> { (3) CO (1) Cl	
C	56.96	56.84
H	2.71	2.84
Cl	24.07	23.85

Metachlorbenzoic anhydride is readily soluble in alcohol, ether, benzol, and chloroform, less easily in ligroine. It crystallizes best from benzol, in the form of yellowish white needles.

### III. *Parachlorbenzoic Anhydride.\**

This substance was prepared from parachlorbenzoic acid, m.pt. 236°, phosphoric anhydride, and benzol, in the same manner as the ortho and meta anhydrides. Like these it is easily soluble in alcohol, ether, benzol, and chloroform, less soluble in petroleum ether. It crystallizes readily from warm benzol in glittering leaflets, which melt at 186°. The analyses gave:—

0.1718 gr. substance gave 0.1648 gr. AgCl.  
 0.2011 gr. gave 0.4185 gr. CO<sub>2</sub> and 0.0590 gr. H<sub>2</sub>O.

Calculated for		Found.
C <sub>8</sub> H <sub>4</sub>	{ (1) Cl (4) CO >O C <sub>8</sub> H <sub>4</sub> { (4) CO (1) Cl	
C	56.96	56.75
H	2.71	3.26
Cl	24.07	23.71

### ANHYDRIDES OF THE MONOBROMBENZOIC ACIDS.

The anhydrides of ortho, meta, and parabrombenzoic acids were prepared from the acids in a similar manner. The orthobrombenzoic

\* The parachlorbenzoic acid used in this experiment, as well as the para-brombenzoic acid, to be mentioned later, were kindly furnished us by Prof. C. L. Jackson of the Harvard College Laboratory, to whom we would here express our warmest thanks for both preparations.

acid employed was obtained from anthranilic acid by means of the Sandmeyer\* reaction, which, as in the case of the metachlor acid above mentioned, we found admirably adapted to our purpose.

*I. Orthobrombenzoic Anhydride.*

Crystallizes from ligroine in fine, white, prismatic needles melting at  $141^{\circ}$ . Readily soluble in ether and chloroform, less easily in benzol, alcohol, and ligroine. The analyses gave :—

0.1663 gr. substance gave 0.1615 gr. AgBr.  
0.1832 gr. gave 0.2928 gr.  $\text{CO}_2$  and 0.0390 gr.  $\text{H}_2\text{O}$ .

Calculated for		Found.
$\text{C}_6\text{H}_4 \left\{ \begin{array}{l} (1) \text{Br} \\ (2) \text{CO} \end{array} \right.$	$\text{C}_6\text{H}_4 \left\{ \begin{array}{l} (2) \text{CO} \\ (1) \text{Br} \end{array} \right. \text{O}$	
C	43.75	43.58
H	2.09	2.36
Br	41.67	41.32

*II. Metabrombenzoic Anhydride.*

Crystallizes from benzol in glittering white leaflets melting at  $97^{\circ}$ . Readily soluble in ether and chloroform, less easily in alcohol, benzol, and ligroine. The analyses gave :—

Calculated for		Found.
$\text{C}_6\text{H}_4 \left\{ \begin{array}{l} (1) \text{Br} \\ (3) \text{CO} \end{array} \right.$	$\text{C}_6\text{H}_4 \left\{ \begin{array}{l} (3) \text{CO} \\ (1) \text{Br} \end{array} \right. \text{O}$	
C	43.75	43.50
H	2.09	2.10
Br	41.67	41.55

*III. Parabrombenzoic Anhydride.*

Crystallizes from benzol in thick prisms, from chloroform in small tablets. Is decidedly more insoluble in the common organic solvents than either the ortho or the meta isomer. Melting point  $212$  to  $213^{\circ}$ . This body has already been described by Jackson and Rolfe; † we have therefore considered an analysis unnecessary.

\* Ber. d. ch. G., XVIII. 1495.

† These Proceedings, XXII. 256.